

# REPORT DOCUMENTATION PAGE

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MEMORANDUM FOR IN-HOUSE PUBLICATIONS

FROM: PROI (TI) (STINFO)

30 Apr 98

SUBJECT: Authorization for Release of Technical Information, Control Number: AFRL-PR-ED-TP-1998-091  
Simon Tam and Mario Fajardo "CO/pH<sub>2</sub> - a Molecular Thermometer"  
HEDM Conference Presentation (Statement A)

# CO/pH<sub>2</sub> -- a Molecular Thermometer

**Simon Tam and Mario E. Fajardo**

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(AFRL/PRSP Bldg. 8451, Edwards AFB, CA 93524-7680)

We utilize reversible temperature dependent changes in the infrared absorption spectrum of CO molecules in solid parahydrogen (pH<sub>2</sub>) to probe the temperature profiles of the matrices during deposition. The intensity of a well-resolved absorption feature near 2135 cm<sup>-1</sup> shows a monotonic increase with temperature over the 2 to 5 K range. The initial state of this transition is estimated to be 7.9(±0.5) K above the ground state of CO/pH<sub>2</sub>. During the deposition of 100 PPM CO/pH<sub>2</sub> samples, we detect temperature gradients of ~ 10 K/cm in samples subjected to estimated heat loads of ~ 10 mW/cm<sup>2</sup>. The resulting estimated thermal conductivities of ~ 1 mW/cm-K (0.1 W/m-K) are four orders of magnitude lower than the conductivity of single crystal solid pH<sub>2</sub>, and more than an order of magnitude lower than previously measured for pH<sub>2</sub> solids doped with 100 PPM concentrations of heavy impurities [V.G. Manzhelli, et al., Low Temp. Phys. v22, p131 (1996)].

20021122 006

# High Energy Density Matter (HEDM) Cryosolid Propellants

## Objectives

- \* Trap 5% molar concentration of energetic additives in solid hydrogen.
- \* Demonstrate size-scalable sample production method.

## Payoffs

### Increased Specific Impulse

$$I_{sp} \propto \sqrt{\Delta H_{sp}}$$

$$\text{LOX/LH}_2 : I_{sp} = 390 \text{ s}$$

$$5\% \text{ B/H}_2 + \text{LOX} : I_{sp} = 500 \text{ s (+30\%)*}$$

\* calculated for  $P_{\text{chamber}} = 1000 \text{ PSIA}$ ,  $P_{\text{exhaust}} = 14.7 \text{ PSIA}$

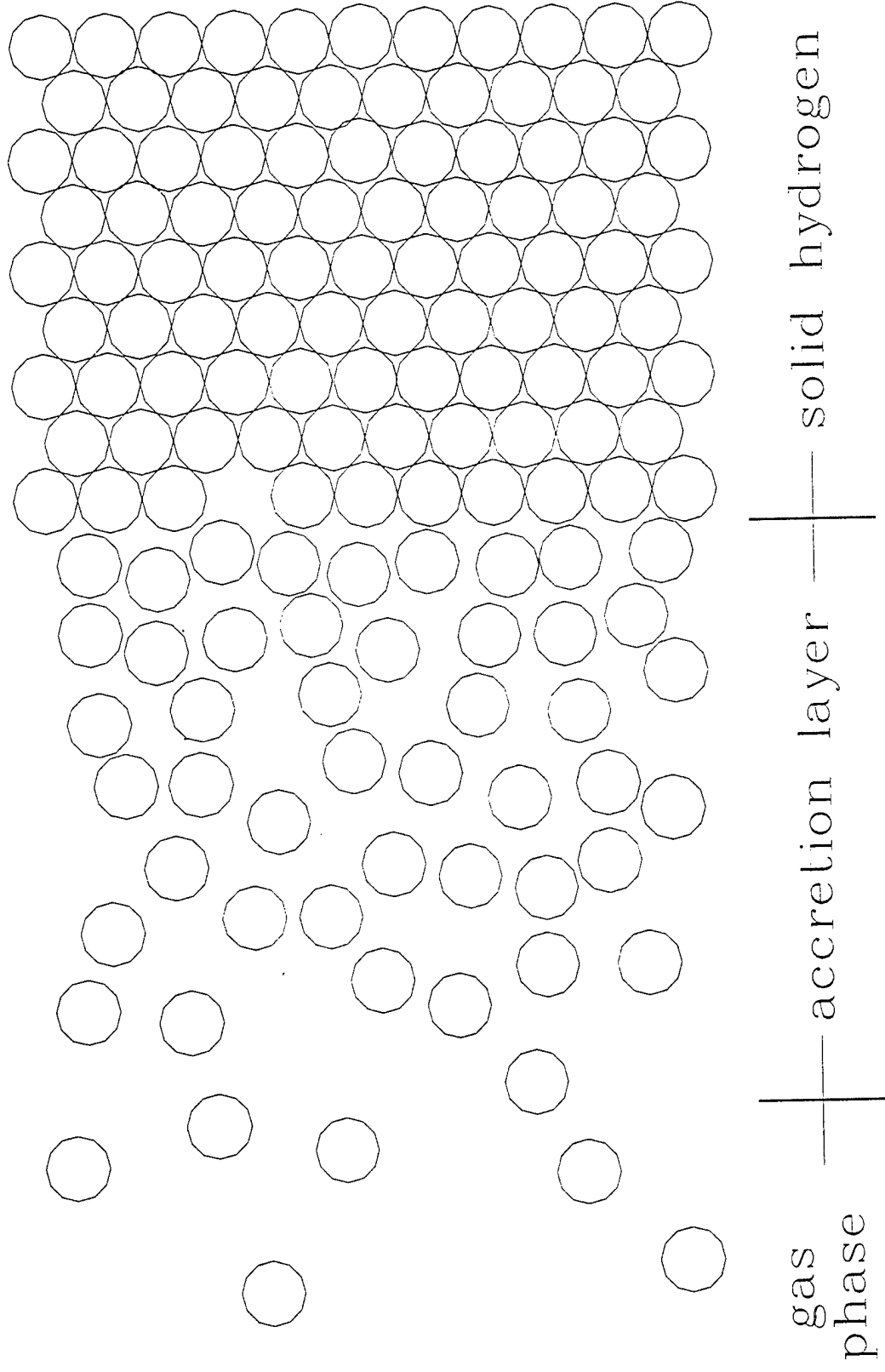
### Greater Propellant Density

$$\text{liquid H}_2 : \rho = 0.070 \text{ g/cm}^3$$

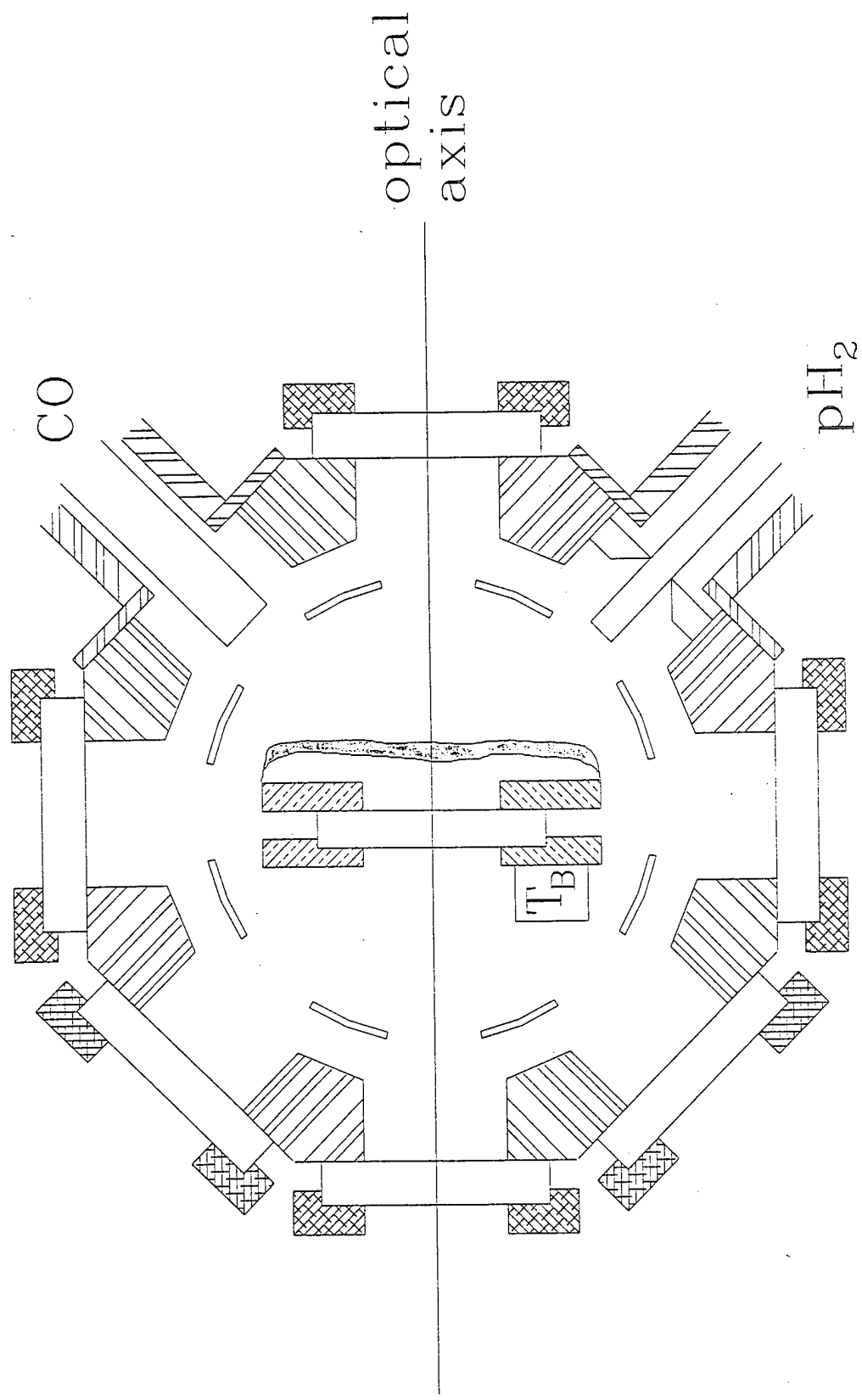
$$\text{solid H}_2 : \rho = 0.087 \text{ g/cm}^3 (+25\%)$$

$$50/50 \text{ liquid He/solid H}_2 : \rho = 0.105 \text{ g/cm}^3 (+50\%)$$

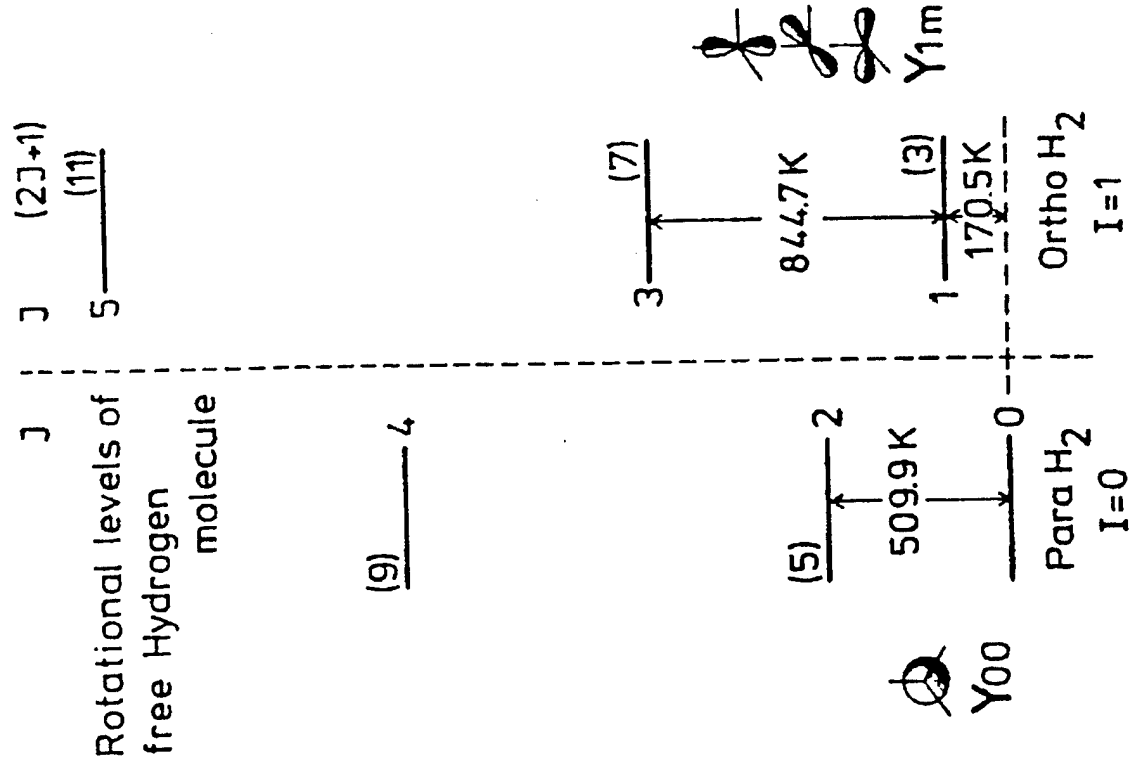
# Deposition Cartoon



## Experimental Diagram – Sample Deposition

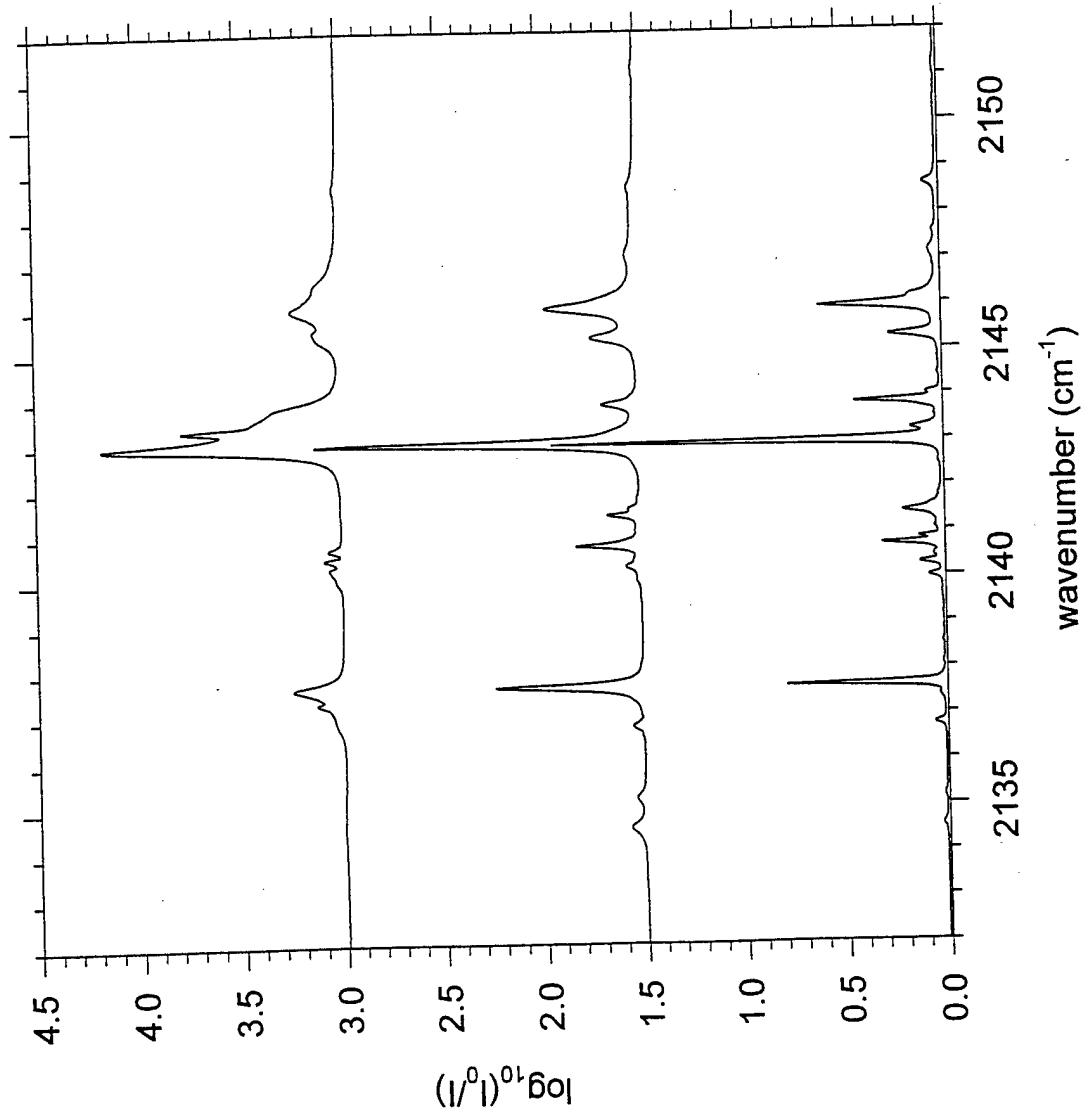


# Ortho and Para Hydrogen



I.F. Silvera,  
Rev. Mod. Phys. **52**, 393 (1980).

# IR Absorptions of CO/pH<sub>2</sub>



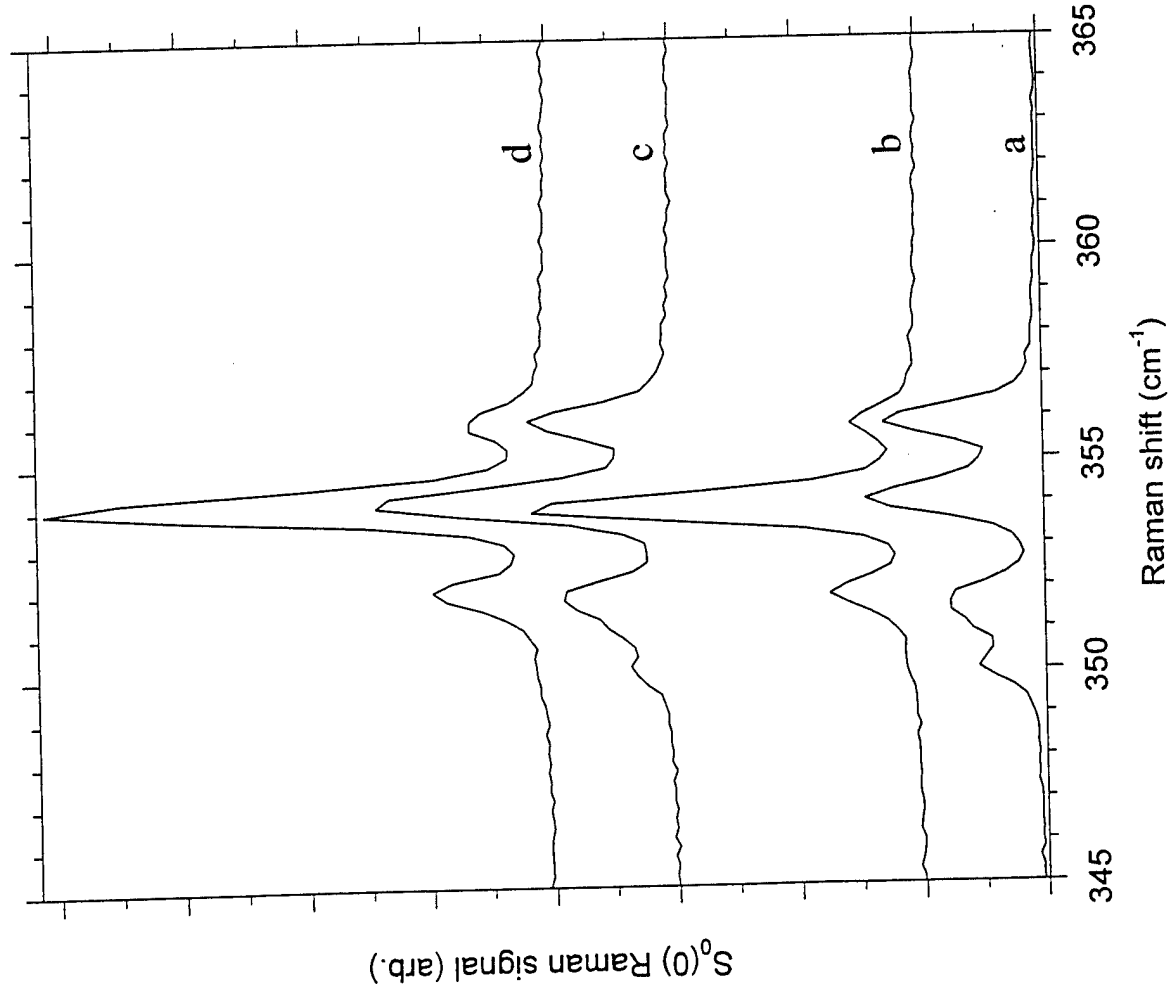
75 PPM CO/pH<sub>2</sub>  
d = 1.7 mm  
resolution = 0.1  $\text{cm}^{-1}$

as deposited at 2 K  
(probably hcp+fcc)

warmed to 4 K

after anneal, at 2 K  
(pure hcp?)

# Raman Spectra of 4.5 and 6 mm Thick Parahydrogen Solids



Mixed hcp/fcc as-deposited structure, anneals to hcp; compare with:

G.W. Collins, et al., Phys. Rev. B **53**, 102 (1996).

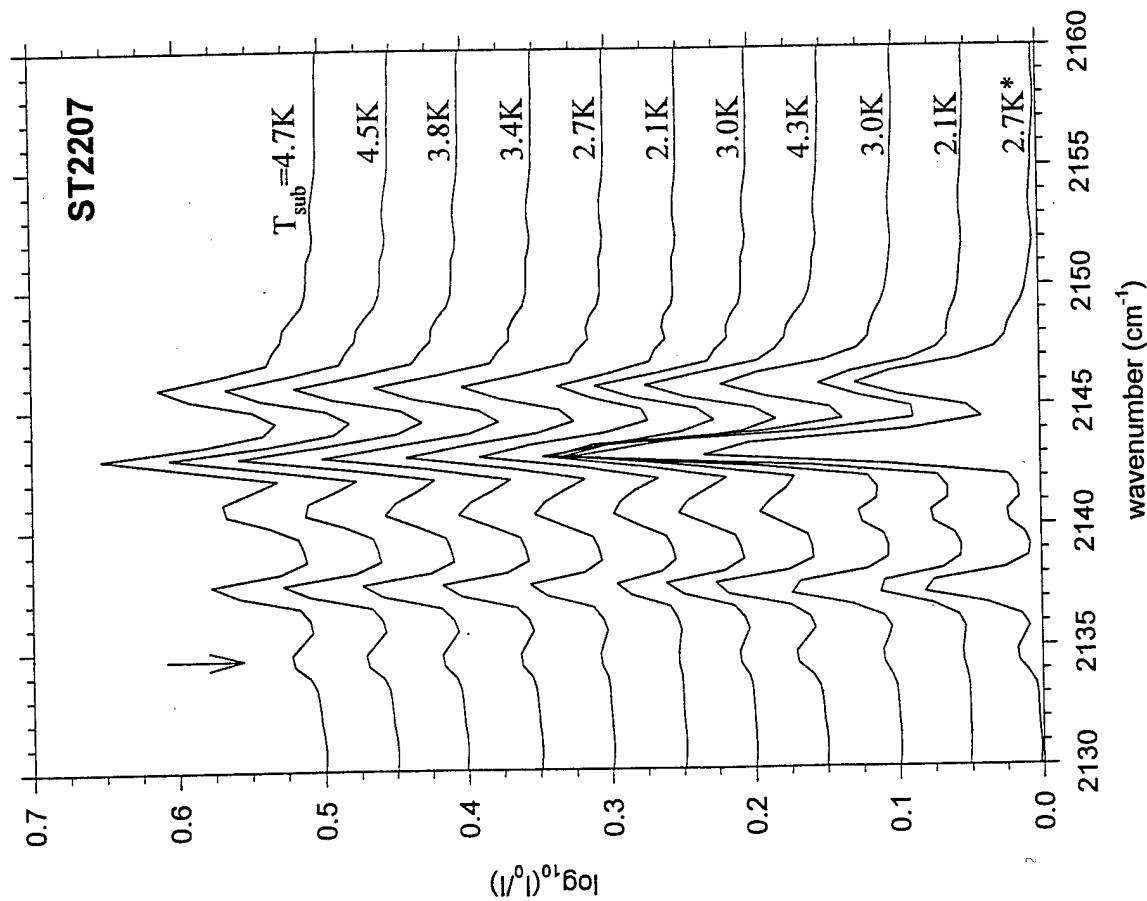
(d) sample in (c) warmed to 4.5 K.

(c) 4.5 mm sample as deposited at 3.3 K ( $\Phi = 290$  mmol/hr).

(b) sample in (a) warmed to 4.5 K.

(a) 6 mm sample as deposited at 3.1 K ( $\Phi = 200$  mmol/hr).

# Reversible Temperature Dependence of CO/pH<sub>2</sub> Spectrum

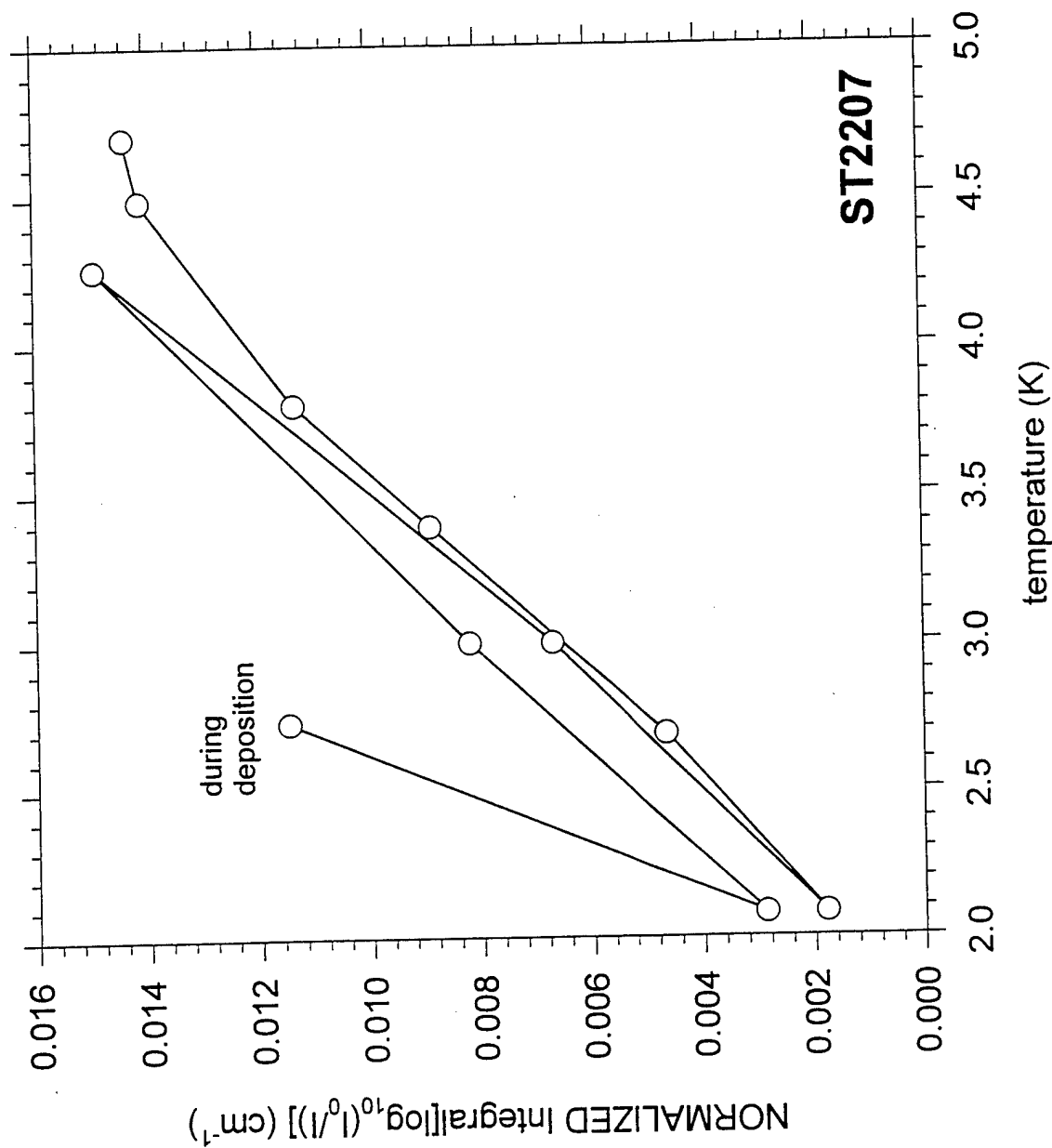


time sequence from bottom to top

lower trace shows spectrum obtained during deposition, other spectra obtained after deposition at various substrate temperatures

arrow indicates "2135 cm<sup>-1</sup> band"

# Intensity of 2135 $\text{cm}^{-1}$ band vs. Temperature

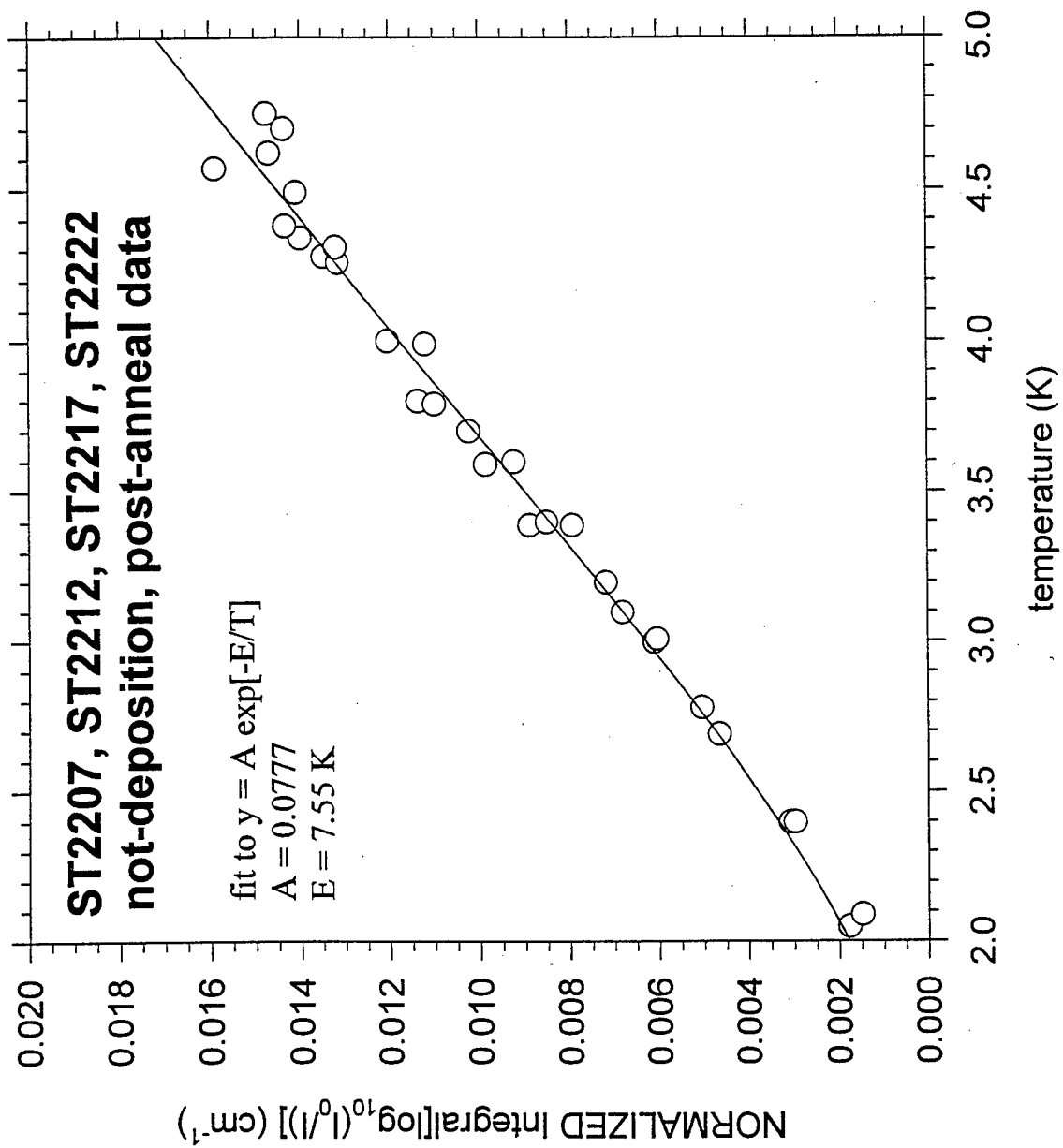


0.9 mm  $\text{CO/pH}_2$  layer deposited on top of 1.9 mm pure  $\text{pH}_2$  layer.

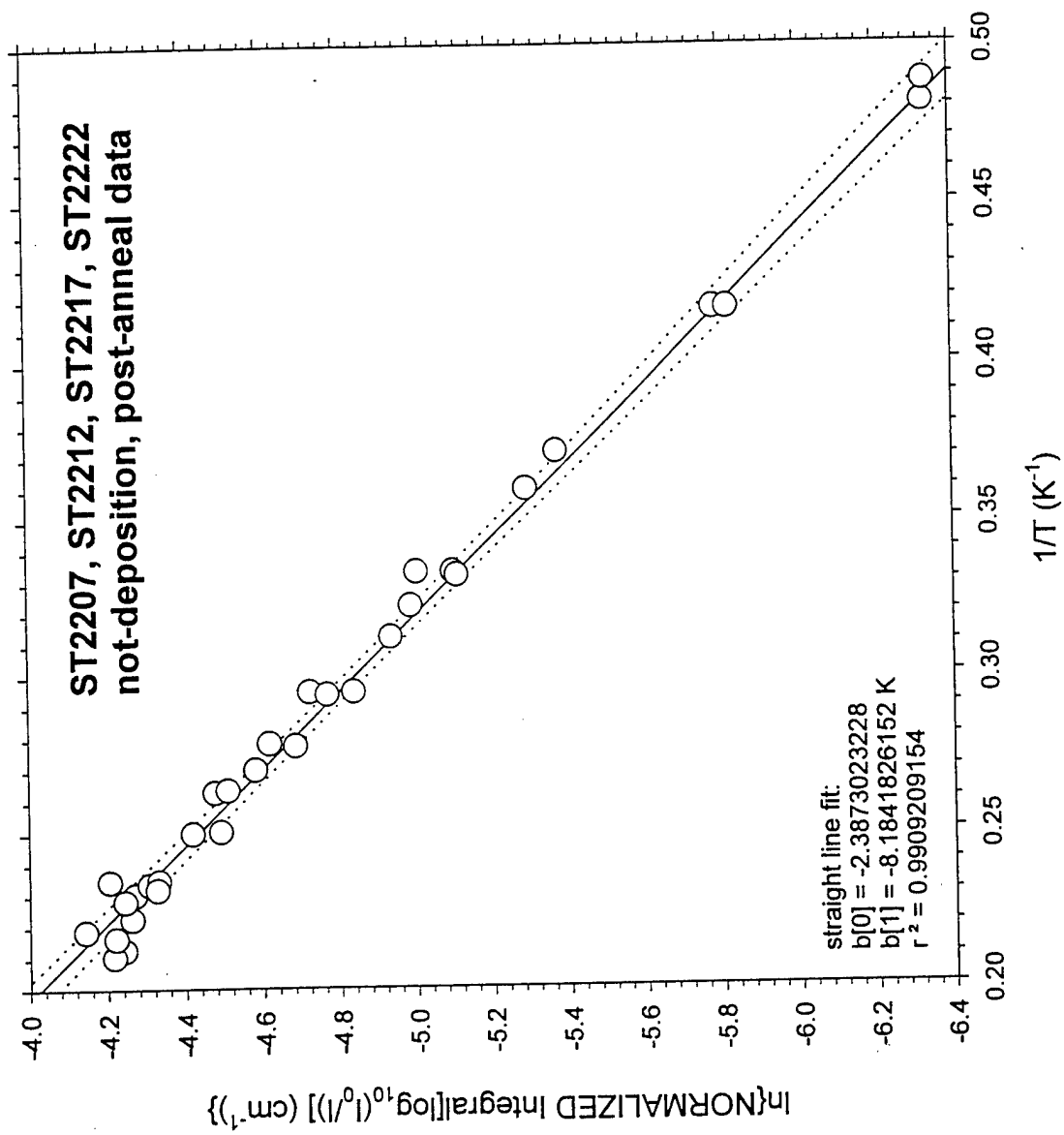
Integrated intensity of 2135  $\text{cm}^{-1}$  band normalized to integral over entire CO band for as-deposited sample.

Irreversible shift upon annealing attributed to fcc  $\rightarrow$  hcp conversion (introduces T measurement error  $\approx +0.2$  K).

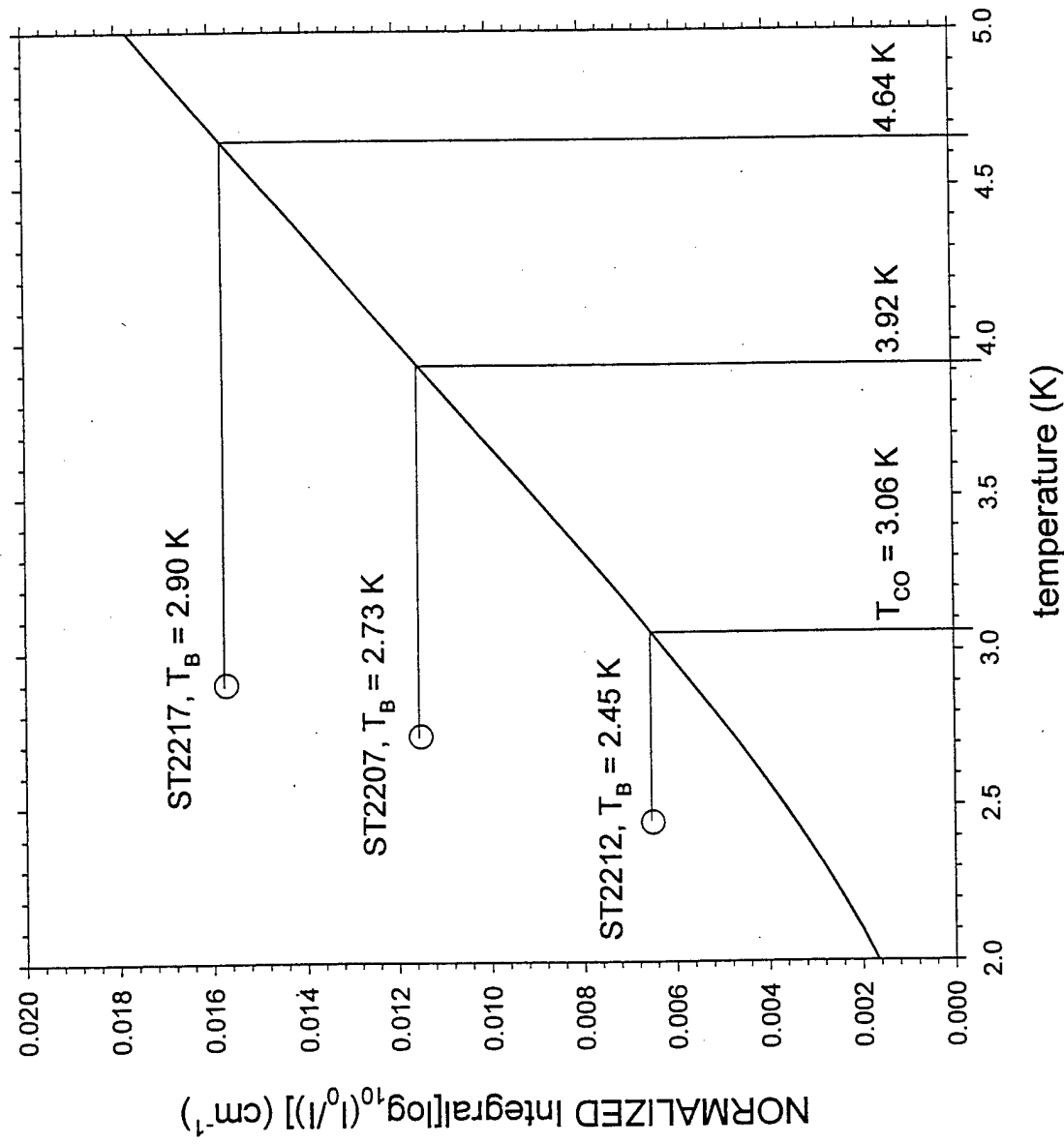
# CO/pH<sub>2</sub> Calibration vs. Si Diodes



# “Van’t Hoff Plot”



# Substrate and Bulk Hydrogen Temperatures During Deposition



“thermometer curve:”

$$y = A \exp[-E/T]$$

$$A = 0.08602$$

$$E = 7.896 \text{ K}$$

Prior to depositions

$$T_B = 1.89(\pm 0.02) \text{ K}$$

After depositions

$$T_B = 2.08(\pm 0.05) \text{ K}$$

pH<sub>2</sub> inlet & deposition rates:

ST2212: 110 mmol/hr

26  $\mu\text{m}/\text{min}$

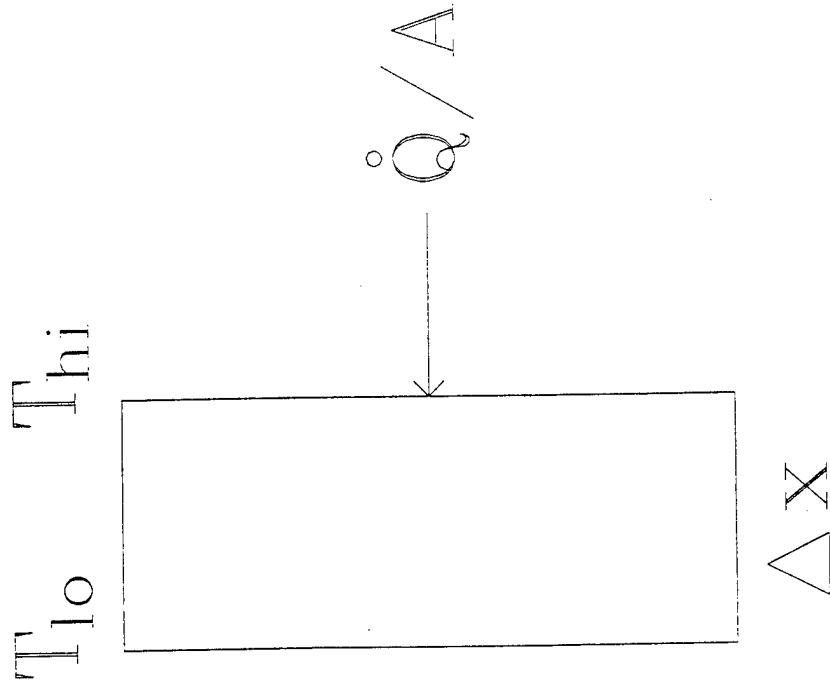
ST2207: 200 mmol/hr

48  $\mu\text{m}/\text{min}$

ST2217: 240 mmol/hr

55  $\mu\text{m}/\text{min}$

## 1-D Heat Transfer



$$\dot{Q}/A = -\kappa \Delta T / \Delta x$$

$$\Delta T = T_{hi} - T_{lo}$$

$\kappa$  is the thermal conductivity

units:

$$\dot{Q}/A \text{ (mW/cm}^2\text{)}$$

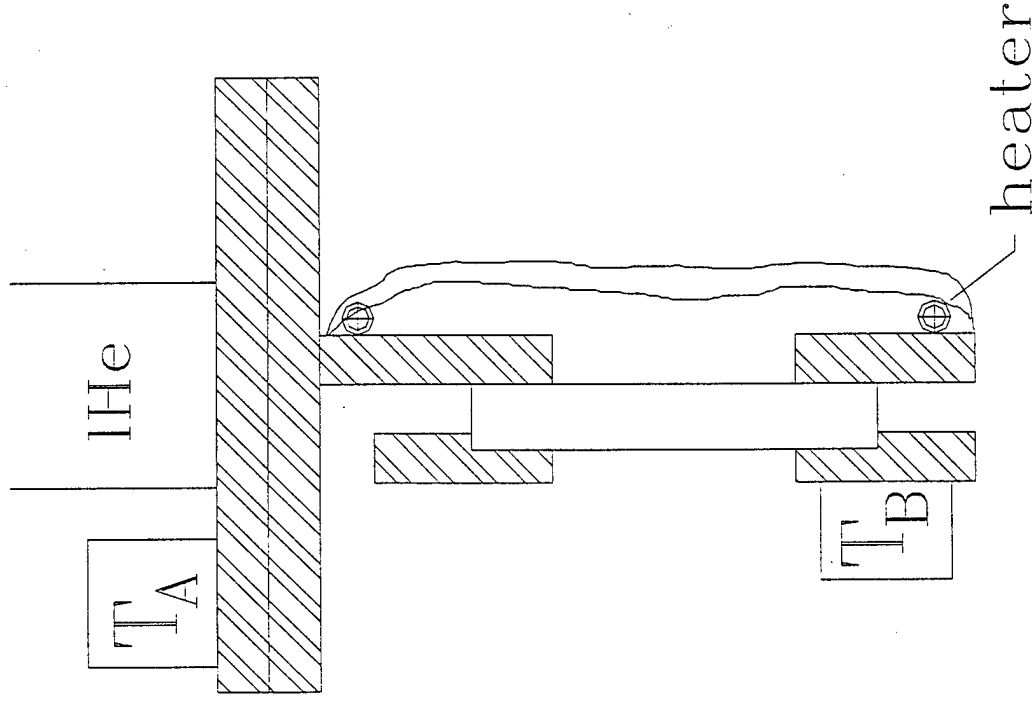
$$\Delta T \text{ (K)}$$

$$\Delta x \text{ (cm)}$$

$$\kappa \text{ (mW/cm-K)}$$

note:  $1 \text{ mW/cm-K} = 0.1 \text{ W/m-K}$

## Experimental Diagram – Heat Flux Calibration

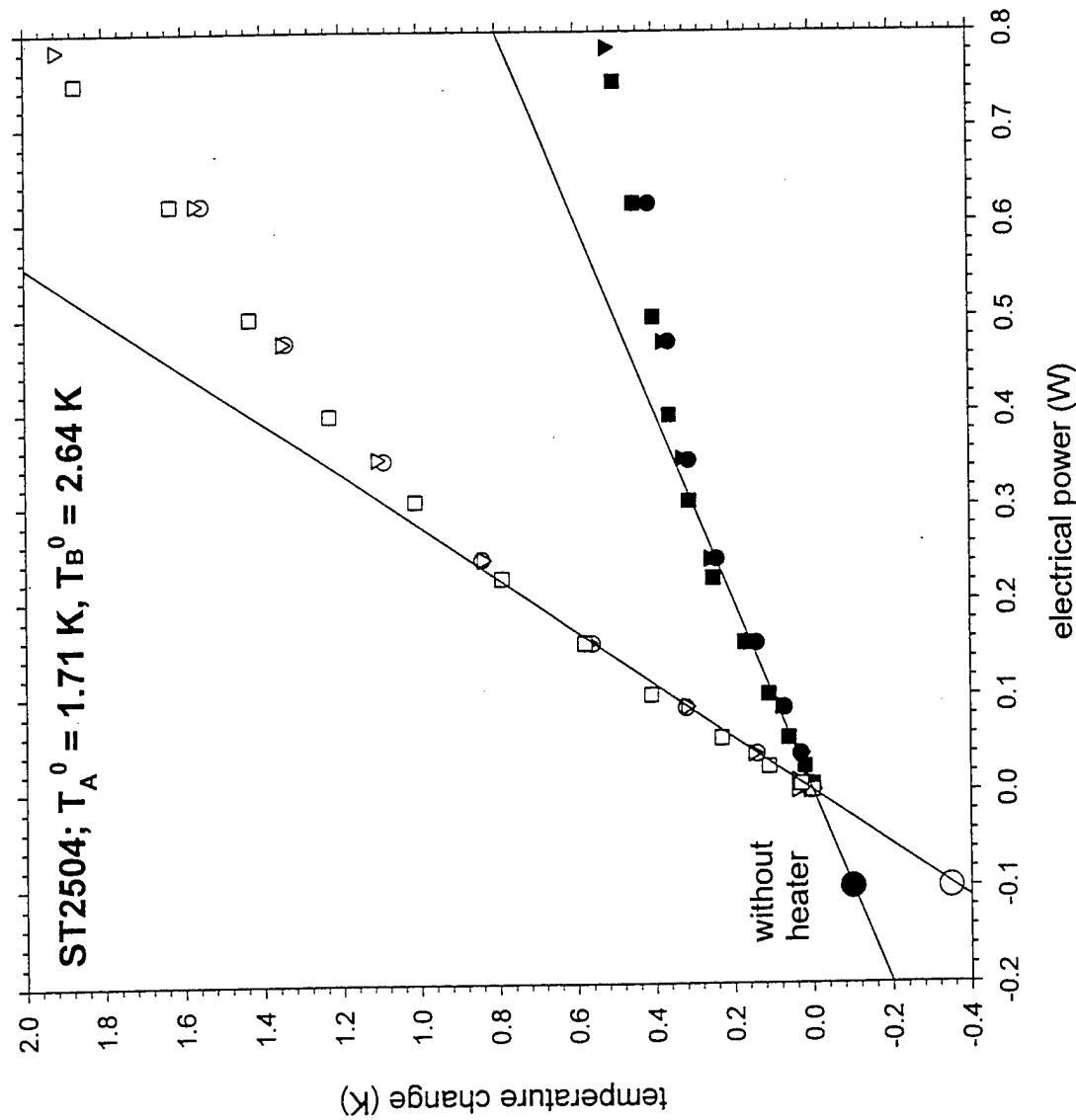


Mimic deposition heat load on substrate holder by using an electrical heater (loop of nichrome wire glued to substrate holder).

Monitor response of Si diode temperature sensors at positions A and B.

Match observed temperature rises during electrical heating and during depositions to estimate heat fluxes during depositions.

# Thermal Response of IHe Cryostat



$T_A$  closed symbols  
 $T_B$  open symbols

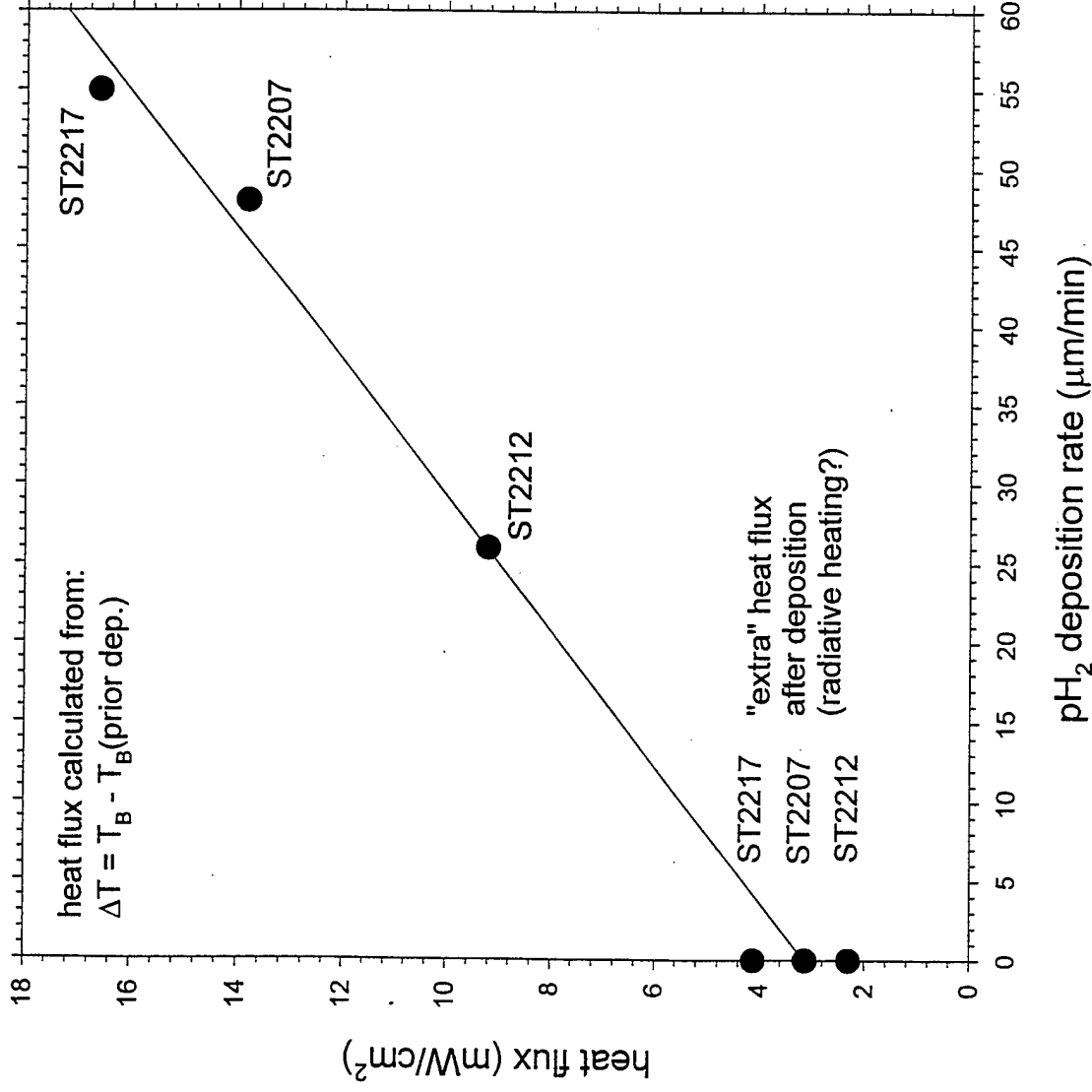
Slopes:

$T_A$ : 1.0 K/W

$T_B$ : 3.6 K/W

Minimum temperatures  
 without electrical heater fit  
 same trend assuming  
 100 mW heat load through  
 phosphor-bronze leads.

# Calculated Heat Flux vs. pH<sub>2</sub> Deposition Rate



Total deposition heat fluxes:  
 ST2212 9.2 mW/cm<sup>2</sup>  
 ST2207 13.8 mW/cm<sup>2</sup>  
 ST2217 16.6 mW/cm<sup>2</sup>

Total – extra:

ST2212 6.9 mW/cm<sup>2</sup>  
 ST2207 10.7 mW/cm<sup>2</sup>  
 ST2217 12.5 mW/cm<sup>2</sup>

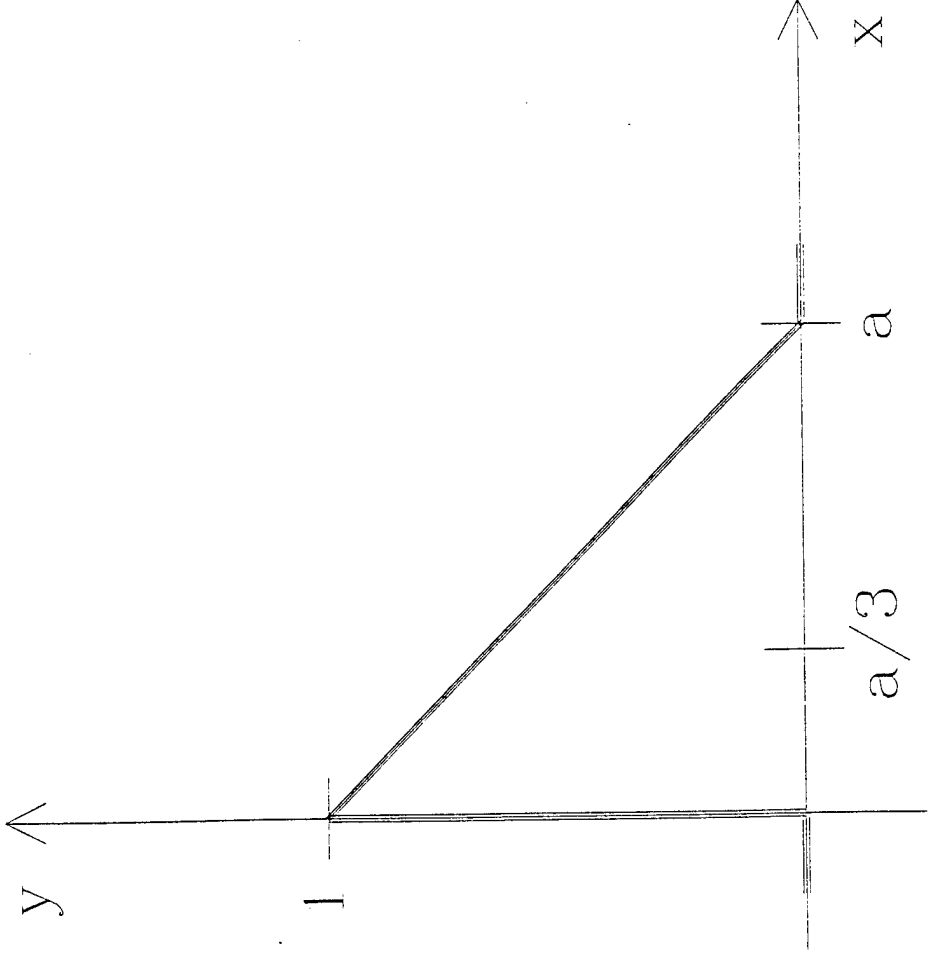
Slope of fit line  $\Rightarrow$

$$E_{\text{dep}}(\text{pH}_2) = 3.25 \text{ kJ/mol} \quad (390 \text{ K})$$

Compare with:

$$E_{\text{sub}}(\text{pH}_2) = 0.9 \text{ kJ/mol} \quad (110 \text{ K})$$

## Time-Weighted Average Position of CO Thermometer



$$y = 1 - x/a$$

$$\bar{x} = \int xy dx / \int y dx$$

$$= \int_0^a (x - x^2/a) dx / \int_0^a (1 - x/a) dx$$

$$= (x^2/2 - x^3/3a) \Big|_0^a / (x - x^2/2a) \Big|_0^a$$

$$= (a^2/2 - a^2/3) / (a - a/2)$$

$$= a^2/6 / a/2$$

$$= a/3$$

## Thermal Conductivity of Rapid Vapor Deposited pH<sub>2</sub>

Expt.	$[T_{\text{co}} - T_{\text{B}}] \text{ (K)}$	$\Delta x \text{ (cm)}$	$\dot{Q}/A \text{ (mW/cm}^2\text{)}$	$\kappa \text{ (mW/cm-K)}$	$\kappa \text{ (W/m-K)}$
ST2212	0.61	0.12	9.2	1.8	0.18
ST2207	1.19	0.22	13.8	2.6	0.26
ST2217	1.74	0.25	16.6	2.4	0.24

Expt.	$[T_{\text{co}} - T_{\text{B}}] \text{ (K)}$	$\Delta x \text{ (cm)}$	$\dot{Q}/A \text{ (mW/cm}^2\text{)}$	$\kappa \text{ (mW/cm-K)}$	$\kappa \text{ (W/m-K)}$
ST2212	0.61	0.12	6.9	1.4	0.14
ST2207	1.19	0.22	10.7	2.0	0.20
ST2217	1.74	0.25	12.5	1.8	0.18

## Summary

Absorption spectrum of  $\sim 100$  PPM CO/pH<sub>2</sub> shows reversible temperature dependent changes which can be used to measure the temperature of the bulk pH<sub>2</sub> during sample deposition.

During a typical rapid deposition ( $R \approx 50$   $\mu\text{m}/\text{min}$ ), the substrate temperature rises about 1 K, and the pH<sub>2</sub> bulk temperature rises about another 1 K in  $\sim 0.1$  cm thick samples.

Heat flux during a typical rapid deposition is  $\sim 10$  mW/cm<sup>2</sup>. This value is about 3x larger than the lower limit estimated from the heat of sublimation of solid pH<sub>2</sub>.

Calculated thermal conductivities are  $\sim 1$  mW/cm-K, about an order of magnitude smaller than previously measured for doped samples grown in an enclosed cell near 10 K.

Our lower thermal conductivities remain unexplained; speculations include:  
polycrystalline nature of our samples,  
random-stacked close-packed microscopic structure,  
systematic errors in our measurements.

Future efforts will include a more careful analysis of possible errors due to radiative heating and other effects.